I.

THE OSMOTIC PRESSURE

OF CANE-SUGAR SOLUTIONS.

II.

THE SEMIPERMEABLE MEMBRANE

OF COPPER COBALTICYANIDE.

D I S S E R T A T I O N

By

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I. THE OSMOTIC PRESSURE OF CANE-SUGAR SOLUTIONS.

INTRODUCTION.

The importance to the science of chemistry of the measurement of osmotic pressure can not be overestimated. It was from a study of the results obtained by Pfeffer, and others, that Van't Hoff was led to put forward the hypothesis that dilute solutions obey the gas laws. Whether the analogy between solutions and gases holds for concentrated solutions could be determined only by the measurement of the osmotic pressure of such solutions. But the difficulties connected with the measurement of the osmotic pressure of concentrated solutions have seemed almost insurmountable. Attempts to repeat even the measurements of Pfeffer have generally failed.

Osmotische Untersuchungen (1877).

Ztschr. phys. Chem., 1., 481, (1887).

The study of osmotic pressure was begun in this laboratory by Morse and Horn   in 1901.   They discovered that a semipermeable membrane could be deposited much more satisfactorily by the electrolytic method than by the diffusion method of Pfeffer.

With a membrane of copper ferrocyanide they measured pressures up to 4.5 atmosphere.   Failure to measure greater pressures was due principally to inability to secure the manometer in the cell.

The following year Morse and Fraser made great improvements in the arrangements for securing the manometer in the cell, and also in the construction and assembling of the parts of the cell.   As a result of this progress they were able to attain a pressure of about 21.5 atmospheres with a normal solution of cane sugar.

But it soon became apparent that the real difficulty lay in obtaining a proper support for the membrane. This problem was then taken up systematically in the laboratory with the result that a number of most satis-

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factory cells have been obtained.

The difficulties being thus far overcome, a careful determination of the osmotic pressure of solutions of cane-sugar was undertaken last year by Morse and Frazer. The results of their work were published   under the title, "The Osmotic Pressure and Freezing-Points of Solutions of Cane-Sugar."   From their measurements of the osmotic pressures of solutions ranging in concen- tration from 0.05 to 1.00 gram-molecular weight of sugar, in 1000 grams of water, they found that the hypothesis of Van't Hoff holds provided the standard for the solvent is the fixed mass of 1000 grams of water. Their conclusions were summed up as follows: "Cane- sugar, dissolved in water, exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state." That is to say, cane-sugar dissolved in water exerts an osmotic pressure throughout the larger volume of the

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solution equal to that which it would exert, as a gas,
if confined to the smaller volume of the pure solvent.
The experimental error in their measurements was too
great to admit of deciding whether the correct standard
for osmotic pressure is the volume of the solvent at
the temperature of maximum density, or at the temperature
at which the pressure is measured.

To test the accuracy of the inferences above
drawn it is evident that very exact determination of
osmotic pressure is demanded.   While the results
published in the above paper were as exact as experi-
mental conditions at that time would permit, the authors
were fully aware of the fact that more precise results
could be obtained by eliminating or obtaining better
control of certain sources of error which necessarily
beset their work.   In the above mentioned paper will
be found the following statement, "The measurement of
the osmotic pressure of cane-sugar solutions will,
therefore, be repeated at an early date, and an attempt
will then be made to improve the procedure in various
ways, with a view to testing more thoroughly the
inferences drawn from the results of the previous work."

It was suggested by Professor Morse that, in fulfilment of this promise, a number of the measurements previously made be repeated under the more favorable conditions that now exist.   Part I. of this paper contains an account and record of the results for five different concentrations.   It should be mentioned here that the coöperation of two parties is absolutely essential in carrying out measurements of osmotic pressure, and that in this work the author has had associated with him Mr. V. L. Kennon, who has been engaged in the same line of work.

The sources of error to which particular attention was called in the above paper of Morse and Frazer were: (1) The "thermometer effects," (2) the uncertainty regarding the true volume of the upper end of the monometer, and (3) the inversion of sugar which takes place in the cell.   These difficulties will be discussed in separate parts of this paper.   How and to what extent they have been overcome will there be described.

T H E   C E L L .

As has already been stated the preparation of a porous cell suitable for the measurement of osmotic pressure has been a problem of the greatest difficulty.   In great measure the problem remains yet unsettled, but so much has been accomplished in the evolution of the cell that it has been possible to produce in the laboratory a number of cells of almost perfect character.

The Construction and Assembling of the

Parts of the Cell.— The details of the construction and assembling of the parts of the cell have been given in previous communications.   In Figure 1. the porous cell is designated by A.   By

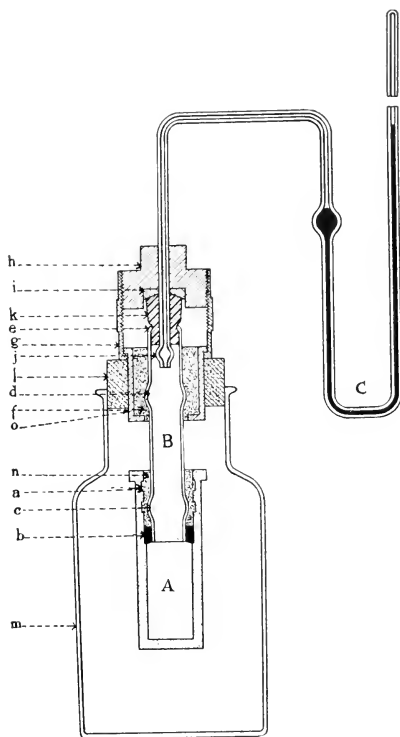Amer. Chem. Jour., 28, 1; 34, 1.

Fig. I.

means of a swiftly revolving carbonendum disk, the
cell while slowly turning in a chuck on the lathe is
ground internally to a distance from the open end of
about one-half its length.   The grinding is continued
until a shoulder is formed entirely around the cell of
sufficient width to support the soapstone ring b.
The letter a designates one of two channels which
serve to give support to the cement.

The hard glass tube B which connects the cell with
the manometer has the enlargements c and d, which are
very necessary to prevent the tube from being pushed
out through the cement of the cell or of the metal
piece o.   At e the tube is contracted so as to give a
better hold on the rubber stopper k.   For this glass
connection the greatest care must be exercised to
select a piece of tubing of the greatest strength and
toughness.   The frequent fracturing of this tube,
usually the constricted end, has been the cause of
much loss of time and labor in our work.

The soapstone ring b is bored and turned out on the
lathe until it will fit closely over the end of the
glass tube and in its place in the cell.   Its lower

end is beveled inward to prevent the lodgment of air.

After the ring has been put in its place on the
tube, the end of the glass tube and the beveled side
of the soapstone ring are covered with molten shellac.
The tube and ring in an inverted position are then
placed in an air-bath and heated at 110° for about
five hours, and then one hour longer at 120°.   Any
space between the tube and the ring is thus filled with
the shellac, and a tight joint obtained.   The addition
of shellac is continued until a covering of considera-
ble thickness is obtained.   The whole of the ground
surface in the interior of the cell is then painted
several times with a dilute solution of rubber in
carbon bisulphide.   The end of the glass tube and the
soapstone ring are painted in the same way, and the
ring carefully inserted in its place in the cell.   The
whole interior surface above the ring is again painted
and the rubber vulcanized by heating in the air-bath.
To insure further against leaks, shellac is then melted
in the bottom of the cavity and painted with rubber
solution.

The purpose of the painting with rubber is to
effectually protect the cement from any contact with

the solution in the cell or the water outside.   The
cement used is a mixture of lead oxide and glycerine
containing about 10 per cent. of water.

The four brass pieces, o, g, h, and i serve to
hold the stopper and manometer in the cell.   The
piece o is bound to the tube B by the litharge-glycerine
cement.

The collar g is provided with an interior
flange which locks with the exterior flange of o.   The
nut h is threaded to fit the interior thread of g.
The brass piece i is concave at the bottom where it
rests upon the stopper.   This serves to prevent the
stopper from moving in any other direction than toward
the interior of the cell.   The holes h and i through
which the manometer passes must be sufficiently large
to allow considerable play for the manometer.
Otherwise the manometer may be broken when the nut h
is screwed down.   The cork ring l holds the cell in
its place in the bottle containing the water in which
the cell is immersed.

The cell used in making the greater part of the
measurements recorded in this paper will be designated

as G.   This cell before burning had a length of 9.12
cm., an external diameter below the rim of 3.58 cm.,
and an internal diameter at the open end of 2.51 cm.
After burning its length was 8.25 cm, internal diameter
at the open end 2.28 cm., external diameter just below
the rim 3.20 cm., and external diameter at the bottom
2.60 cm.   The cell tapered .044 cm. per cm. of length.
Its total capacity after the assembling of all its
parts was 16.1 cc.

The Preparation and Development of the Membrane.-

On account of the almost ideal character of
cell G the history of the preparation and development
of its membrane will be given.

The air was removed from the cell walls by the
usual method of endosmose.   The electrodes were both
of platinum.   For cells of very fine texture a 0.005
normal solution of lithium sulphate is used instead of
a solution of potassium sulphate of the same concen-
tration on account of the higher rate of endosmose of
the former solution.   With a current pressure of 110
volts the endosmose for G was less than 40 cc. per hour.

After about 500 cc. of water had passed through the
walls the sulphate solution was replaced by distilled
water and the electrolysis continued until all the
sulphate was removed from the cell.   The cell was then
filled with recently boiled distilled water and placed
in a vessel of the same until it was desired to deposit
the membrane.

In depositing the membrane of copper ferrocyan-
ide in the cell the method of Morse and Horn was followed.
A description of the form of apparatus in use may be
had in a previous paper.   The anode and cathode
were respectively of copper and platinum.   The solution
of potassium ferrocyanide placed in the cell and that
of the copper sulphate outside were both of 0. 1 normal
concentration.   The former was renewed every few minutes
to prevent the accumulation of alkali and the consequent
injury to the membrane formed.

A current pressure of about 110 volts has been
found the most satisfactory voltage to use in the

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deposition of the copper ferrocyanide membrane. With
a voltage of 108, cell G offered a resistance of
106000 ohms when the electric circuit was first closed.
This great resistance was due no doubt to the pores of
the cell wall being filled with water.   The resistance
soon began to decrease and in exactly one hour from
the time of closing the circuit it had fallen to 22660
ohms.   From this point on the resistance increased
until in 45 minutes more it was 34354 ohms.   After
soaking the cell over night in distilled water the
membrane forming process was continued.   In one hour
the resistance had reached 107400 ohms when it began
to fall slightly.   The cause of this falling after a
time is not known, although it has often been observed.

At this point the cell was again soaked in
distilled water until the next day when after less than
two hours with a voltage of 108 the resistance had
risen to 270000 ohms and remained constant.   This
resistance was the highest up to that time obtained with
any cell, and was regarded as the "maximum resistance"
for this cell, although in several instances afterwards
the resistance reached 375000 ohms.   Whenever in any

subsequent reenforcement of the membrane the resistance became constant at 270000 ohms the membrane was considered as certainly ready for a measurement of pressure. However, it has been observed that just as good a measurement can be obtained when a much lower resistance is reached. What resistance a cell and membrane will offer to the current will depend, no doubt, upon a number of conditions. But our experience has been that after a measurement of pressure the soaking of the cell in water for a considerable time, at least twelve hours, is the surest way to obtain a high resistance upon again repeating the membrane forming process. If the process is repeated early after the removal of a sugar solution from the cell it is seldom that the maximum resistance is reached. It has been our plan always after a measurement to soak the cell over night in distilled water before again attempting to reenforce the membrane for another measurement.

If the result of the first deposition of the membrane in a new cell is encouraging, the usual procedure is to set the cell up with a preliminary

solution of sugar of about half-normal concentration.
To this solution is added, in the case of a membrane of
copper ferrocyanide, enough potassium ferrocyanide to
make a tenth-normal solution, and the cell is placed
in a tenth-normal solution of copper sulphate.   This
procedure is thought to strengthen the membrane by a
process of rupture and subsequent mending in weak
places.   It also throws light upon the character of
the cell wall.

     In setting up a cell, after the insertion of
the stopper, a mechanical pressure is brought to bear
upon the cell and its contents by means of the nut and
collar.   In the case of very high concentrations the
nut is repeatedly screwed down until the experimenter
is satisfied that sufficient pressure has been brought
to bear to prevent the removal of the stopper during
the experiment.   This "initial" pressure for high
concentrations is often made equal to 14 or 15
atmospheres, but this pressure is never made equal to
the osmotic pressure of the solution.

     In the preliminary trial with cell C an initial
pressure of about 2.5 atmospheres was brought to bear.

The mercury continued to rise in the manometer until
it indicated a pressure of about 5 atmospheres.   The
mercury then fell.   That the membrane was ruptured
considerably was shown by its low resistance at the
beginning of the next membrane forming process, and
from the fact that after four hours the resistance was
only 93000 ohms.   However, the cell was again set up
as before.and a pressure of about 13 atmospheres was
attained.

The cell was then considered ready for an
exact measurement of pressure, and was set up with a
0.6 weight-normal solution.   After this measurement,
in the difficult operation of removing the stopper from
the cell, the exterior end of the glass tube of the
cell was fractured.

By exercising the greatest care we succeeded
in repairing the break and in about a week the cell was
again ready for use with a membrane resistance of
280000 ohms.

Our experience has been that in the beginning
of the history of a membrane there is considerable
leakage and dilution during a measurement, and for this
cause our first experiments were rendered unreliable
and had to be repeated.

THE MANOMETER.

In Figs. I. and II. are shown the form of
manometer used previous to this work. The manometer
tube had a diameter of bore of about 0.5 millimeter,
and the length of the column of enclosed air was from
400 to 450 millimeters. On the descending limb of
the manometer was blown a bulb to serve as a reservoir
for the mercury, while upon the open end was another
bulb to prevent the manometer from slipping through
the stopper.

This original form was subject to several
serious objections. In the first place, in the very
difficult operation of inserting the manometer in the
cell, the enclosed air was likely to pass the bend in
the tube and escape into the bulb, or the solution
from the cell might get past the mercury into the air
space. As a result of one or the other of these
causes the manometer had to be frequently refilled, an
operation requiring considerable time. This defect

in the original form has been overcome by blowing another bulb in the ascending arm of the manometer directly opposite that in the descending arm. As a result of this improvement our monometers have never required refilling. The manometer is further improved by substituting for the bulb on the open end an enlargement made without increasing the bore of the tube. This renders it less difficult to replace solutions in the manometer, and, further, diminishes the chances of getting air into the bend of the tube, or makes the removal of the same a very simple matter.

But by far the most serious objection to the older manometer lies in the uncertainty regarding the volume of the closed upper end. Since in the measurement of a pressure of about 24 atmospheres, approximately that of a weight-normal solution, the length of the air space is only about 18 millimeters, varying with different manometers, this uncertainty becomes a matter of most serious consequence. This difficulty has been most successfully overcome by replacing the air in the upper end with a thread of mercury. How this is done will be described in connection with the filling of
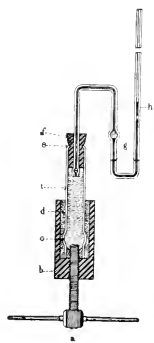
Fig II

the manometer.   The improved form of manometer with
which the measurements here recorded were made is
shown in Fig. IV.

Calibration of the Manometer.-

        The careful calibration of the manometer is a
matter of the greatest importance.   The form of
apparatus for carrying out this calibration is shown
in Fig. II., and has been fully described.   The
method of calibration is similar in principle to that
employed for endiometers.   On the manometer are etched
two lines of reference, one at g (Fig. II.) on the
ascending arm, the other near the top of the manometer.
The calibration, briefly described, is carried out as
follows: After being carefully cleaned and dried the
manometer is filled with pure mercury and connected
with the calibrating apparatus which is also filled
with mercury.   A short thread of mercury (h Fig. II.)
is introduced,leaving a short air space between the
thread and the main column of mercury.   After clamping
the manometer and apparatus in a perfectly vertical
position, the thread of mercury is made to descend until

its lower end is just opposite the line of reference g
which will be designated as Scratch No. 1., or zero-
point.   The length of the thread is then determined
by means of the cathetometer and standard scale.   The
thread is then made to ascend until its lower end
occupies the place previously occupied by the upper end,
and the length again determined.   This procedure of
placing end to end is continued throughout the whole
length to be calibrated.   To verify the calibration a
second or third series of readings is made beginning
with the same fixed point of reference.   There are thus
obtained all the data necessary for plotting the curve
of corrections.

      The manometer is then removed from the calibrat-
ing apparatus and the capillary depression determined
in the usual way.

Filling the Manometer with Pure Air.-

      The next step is to fill the manometer with
pure air.   To do this the lower end of the manometer
is connected with a reservoir of mercury which can be

raised or lowered as desired. Carefully purified air
is then repeatedly drawn in and expelled and finally
the manometer is closed in the following way: Before
drawing in the air which is to be enclosed finally,
the reservoir is raised until the rubber tubing joining
the manometer to the purifying apparatus is partially
filled with mercury. The rubber connection is then
pushed aside with the thumb and finger, breaking the
mercury column. By lowering the reservoir the desired
quantity of air is drawn in, and then after releasing
the rubber connection a thread of mercury of the de-
sired length is made to follow. The thread should be
of such length that it shall eventually fill all space
heated in the operation of sealing off the end of the
manometer. After the thread has been drawn down a few
inches below the top of the manometer, the manometer
can be detached from the air-purifying apparatus, the
mercury thread cutting off all connection between the
enclosed air and that outside. By means of a small
hand blow-pipe a short piece of manometer tubing is
then sealed on to the end of the manometer and the end
of the manometer drawn out to a capillary about 3 or

4 inches in length.   By raising the mercury reservoir
the mercury thread is forced up until it reaches
nearly to the end of the capillary.   The end of the
capillary is then sealed off.

The reservoir is now lowered until there is
considerable diminished pressure, so that in the
subsequent heating the mercury shall not be forced out
of the heated portion.   The end of the manometer and
the mercury filling it are then heated at the point
where it is desired to close the manometer.   The
heating with the blow-pipe will necessarily volatilize
some of the upper end of the thread, and the heat and
vapor will force the thread down some distance from
the place heated, but if the operator is very careful
in his manipulation of the blow-pipe, a good seal may
be obtained, and upon cooling the mercury will resume
its place and completely fill the space in the closed
end of the manometer.   The closing of the manometer
requires the cooperation of two persons, and is a most
difficult operation, but usually after several
failures it can be done quite successfully.

By thus sealing off a thread of mercury in the

upper portion of the manometer all uncertainty as to
volume of air is entirely removed.   It is only
necessary to determine the length of air column between
the thread at the top and the mercury column below,
making the usual correction for double meniscus.   As
this correction is quite considerable for the higher
pressures, it is of course always taken into account.

Determining the Volume of the Enclosed Air.—

        After filling the manometer as above described
it remains to determine the volume of the enclosed air.
This is done by substituting for the reservoir of
mercury a piece of tubing of the same bore as the
manometer and observing the volume of the air under a
number of different pressures, and reducing all
observations to standard conditions.   The distances
between the fixed points designated as Scratch No. 1 and
Scratch No. 2 are then carefully determined once for
all, as is also the relation of the top of the manometer
to the scratches.   Data are thus obtained which render
it possible if desired to use the top of the manometer
also as a point of reference.

Preparation for a Measurement of Pressure,-

To prepare the manometer for a measurement of pressure the open end and enlargement is painted with dilute rubber solution, and the hole in the rubber stopper to be used filled with some of the same solution. The stopper is then slipped over the enlargement to its place on the manometer. Waxed shoemaker's thread is tightly wrapped and tied around the manometer tube just above the enlarged portion as a further precaution against the slipping of the manometer upward through the stopper. This preparation should be made at least the day before the manometer is to be used in order that the rubber shall have time to dry and form a tight connection.

Before inserting the manometer in the cell, the mercury in the descending limb of the manometer, or the solution, if the manometer has been previously used for a measurement, must be replaced by the solution whose osmotic pressure is to be determined. This is accomplished by means of a very simple form of apparatus in the shape of a U-tube filled with the fresh solution, to which suction can be applied after the tube has been attached to the manometer.

This piece of apparatus serves also to remove any air
that may get into the bend of the manometer.

The stopper is then inserted in the cell in
the way described   by Morse and Frazer.   Care is
taken to avoid as far as possible any heating of the
cell and its contents during the operation of setting
it up.   To give rigidity to the protruding end of the
stopper and bind it closer to the manometer, waxed
shoemaker's thread is tightly wound and tied around
the stopper, and over this is wrapped sticky insulating
tape.   The nut is then screwed down on to the stopper
and the cell placed in the bottle of water.

Experimental Data.

The manometer used in this work will be
designated as No. 4. No. 5. and No. 6.   They were

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calibrated according to the method above described.

Manometer No. 4.

Average length of mercury thread used in
    calibration,............................... 15.964 mm.
Weight of mercury thread,................. 0.0409 gram.
Average diameter of bore,................ 0.50 mm.
Distance from Scratch No. 1 to top of
    manometer,...........................477.85 mm.
Distance from Scratch No. 1 to
    Scratch No. 2,......................294.46 mm.
Number of calibration units of air under
    standard conditions in manometer,.461.34
Capillary depression,..................... 0.02 atmosphere.
Correction for double meniscus,.......... 0.17 calibra-
                                                 tion unit.

Total capacity from Scratch No. 1 to
    top,............................... 0.094 cc.

Manometer No. 5.

Average length of mercury thread used
    in calibration,.................... 15.685 mm.
Weight of mercury thread,................ 0.0385 gram.
Average diameter of bore,................ 0.48 mm.
Distance from Scratch No. 1 to top
    of manometer,.....................482.58 mm.
Distance from Scratch No. 1 to
    Scratch No. 2,......................295.94 mm.
Number of calibration units of air,
    under standard conditions, in
    manometer,........................442.18
Capillary depression,..................... 0.02 atmosphere.
Correction for double meniscus,.......... 0.16 calibration
                                                 unit .

Total capacity from Scratch No. 1 to
    top,..... .... 0.088 cc.

Manometer No. 6.

Average length of mercury thread used
  in calibration,................... 13.841 mm.
Weight of mercury thread,.............. 0.062 gram.
Average diameter of bore,.............. 0.64 mm.
External diameter of manometer tube,... 5.1 mm.
Distance from Scratch No. 1 to top,....507.91 mm.
Distance from Scratch No. 1 to
  Scratch No. 2,............... ..382.06 mm.
Number of calibration units of air,
  under standard conditions, in
  manometer,........................402.13
Correction for double meniscus......... 0.21 calibration
                 unit.
Capillary depression,.................. 0.02 atmosphere
Total capacity from Scratch No. 1 to top,0.166 cc.

Since manometer No. 6 has been used in the greater
number of measurements recorded in this paper, the data
for its calibration are given.

   In Table I., column I. gives the actual readings
on the scale, for the first series of observations.
Column II. gives the differences between successive
readings.   In column III. are the actual readings on
the scale, for the second series of observations, and
in column IV. are the differences between successive
readings of the second series.   Column V. contains the
average of the differences of the two series of read-

ings, while in column VI. are given the readings of
the scale that would have been obtained had the zero of
the scale had coincided with that of the manometer.

It will be observed (column VI.) that the dis-
tance covered by 37 lengths of the mercury thread was
512.11 mm.   Dividing 512.11 by 37, we obtain the aver-
age length of thread - 13.841 mm.   The mercury thread
was therefore considered as containing 13.841 calibra-
tion units.   Column VII. gives the multiple of these
values corresponding to the readings contained in col-
umn VI.   In column VIII. are given the differences
between the corresponding values in columns VI. and VI .
These differences are the correction values used in plot-
ting the correction curve.

TABLE I. — Calibration Data for Manometer No. 2.

No. of Lead-ing.	I. Readings upward on scale (first series).	II. Differ-ences.	III. Readings up-ward on scale (second series).	IV. Differ-ences.
1	867.54	13.61	867.54	13.61
2	853.96	13.58	853.96	13.58
3	840.35	13.65	840.35	13.67
4	826.70	13.69	826.68	13.63
5	813.01	13.62	813.00	13.63
6	799.39	13.64	799.37	13.61
7	785.75	13.60	785.76	13.58
8	772.15	13.56	772.18	13.56
9	758.59	13.61	758.62	13.66
10	744.98	13.75	744.76	13.68
11	731.25	13.75	731.08	13.73
12	717.48	13.63	717.35	13.75
13	703.85	13.74	703.60	13.75
14	690.11	13.65	690.08	13.75
15	676.46	13.72	676.43	13.72
16	662.74	13.74	662.71	13.71
17	649.00	13.71	649.00	13.75
18	635.29	13.72	635.25	13.70
19	621.57	13.75	621.55	13.76
20	607.82	13.81	607.79	13.78
21	594.01	13.86	594.01	13.85
22	580.15	13.86	580.16	13.81
23	566.29	13.92	566.35	14.05
24	552.37	13.87	552.30	13.88
25	538.50	13.90	538.42	13.85
26	524.60	13.88	524.57	14.01
27	510.72	13.89	510.56	14.06
28	496.83	14.06	496.50	14.10
29	482.77	14.10	482.40	14.02
30	468.67	14.06	468.38	14.03
31	454.61	14.11	454.35	14.08
32	440.50	14.16	440.27	14.07
33	426.34	14.21	426.20	14.18
34	412.13	14.21	412.02	14.12
35	397.92	14.13	398.00	14.19
36	383.79	14.16	383.81	14.21
37	369.63	14.17	369.60	14.20
38	355.46		355.40	

TABLE I. - Continued.

No. of Read- ing.	V. Average of differ- ences of first and second series.	VI. Readings on scale cal- culated from zero- point.	VII. Product of number of settings by mean length of thread.	VIII. Connec- tion values.
1	13.610	13.61	13.841	7.22
2	13.580	27.19	27.632	0.49
3	13.660	40.85	41.523	0.67
4	13.685	54.53	55.364	0.83
5	13.625	68.16	69.205	1.05
6	13.625	81.78	83.046	1.27
7	13.590	95.37	96.887	1.52
8	13.560	108.93	110.728	1.80
9	13.635	122.57	124.569	2.00
10	13.715	136.28	138.410	2.13
11	13.740	150.02	152.251	2.25
12	13.690	163.71	166.092	2.38
13	13.730	177.44	179.933	2.40
14	13.650	191.09	193.774	2.68
15	13.720	204.81	207.615	2.81
16	13.735	218.54	221.456	2.92
17	13.730	232.28	235.297	3.04
18	13.710	245.98	249.138	3.16
19	13.755	259.73	262.979	3.25
20	13.795	273.53	276.820	3.29
21	13.855	287.38	290.661	3.28
22	13.835	301.22	304.502	3.28
23	13.985	315.20	318.343	3.14
24	13.875	329.08	332.184	3.10
25	13.875	342.95	346.025	3.08
26	13.945	356.90	359.866	2.97
27	13.975	370.87	373.707	2.84
28	14.080	384.95	387.548	2.60
29	14.060	399.01	401.389	2.38
30	14.045	413.06	415.230	2.17
31	14.045	427.10	429.071	1.97
32	14.115	441.22	442.912	1.69
33	14.190	455.41	456.753	1.34
34	14.165	469.58	470.594	1.01
35	14.160	483.74	484.435	0.70
36	14.185	497.92	498.276	0.36
37	14.185	512.11	512.117	0.01
38				

THE REGULATION OF TEMPERATURE CONDITIONS.

The greatest difficulty presenting itself in the exact measurement of osmotic pressure has been the maintaining of constant temperature conditions. Fluctuation in temperature during an experiment is a source of great error and must be eliminated if accurate measurements are to be obtained. This source of error has been designated as <u>thermometer effects</u> and manifests itself in the following way.

If the temperature of the room in which is placed the cell containing a solution whose pressure is being measured falls, the solution and mercury contract faster than the water can pass through the membrane to maintain the pressure which is normal to the solution, and consequently the mercury column falls to a point below that which is normal for the concentration of the solution. If the temperature of the room ceases to fall and remains stationary long enough, water will continue to enter the cell and the mercury will rise to its

normal position and will remain there as long as tem-
perature conditions are unchanged.

On the other hand, if the temperature of the
room rises, the solution and mercury will expand more
rapidly than the water is expelled, and we shall have
too great a rise in the mercury.   But if the maximum
temperature remains constant sufficiently long, event-
ually normal conditions will be restored.   It is only
when the changes in the temperature of the cell contents
are very slow that contraction or expansion can be com-
pensated by the passage of the water through the mem-
brane.

APPARATUS EMPLOYED.

The means by which these temperature fluctu-
ations have been reduced to insignificant proportions
are quite elaborate.   For details the reader is referred
to a communication   which is soon to appear from this
laboratory.

The essential features consist in general of a

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large bath of more than 300 litres of water, and over
this a nearly tight enclosure, in each of which uniform
temperatures are maintained by constant circulation of
the water and of the air, and, enclosing the whole a
much larger structure, in which by means of automatically
regulated electric and gas stoves uniform temperature
conditions are also maintained.

The bath consists of a rectangular copper-lined
wooden box, 1.24 meters long, 0.457 meter wide, and
0.66 meter deep. It is surrounded by a larger
wooden box, the intervening space on all sides except
the top being tightly packed with hair.

The enclosure above the bath has a height of
0.508 meter , a length about three-fourths that of the
bath, and a width slightly greater than that of the
bath. It has a top or cover which is hinged at the
back and which can easily be raised or lowered. It
contains in front a mirror plate glass window hinged
at the bottom. This house contains also double walls
except on the top and in front. As in the case of
the bath the spaces between are jacketed with hair.
The spaces in the framework of the top are filled with

hair held in place by a covering of flannel tacked to
the frame.   The whole top is covered with a hair
mattress.   The glass of the window is completely
covered with a thick flannel-covered pad divided in a
number of places so that by lowering any one of the
curtains thus formed observations can be made without
exposing more than a small section of the window.
Light is thrown into the house from without.   The
enclosure is made as nearly airtight as possible, by
the selection of suitable lumber for its construction,
by the frequent use of an elastic varnish, by sticking
insulating tape over the joints, by enameling heavily
the whole interior, and finally, by making the glass
window to close on the inside against rubber weather
strips.

        The whole bath and house above together with
the cathetometer and scale used in making observations
rests upon supports entirely independent of the floor
or other woodwork of the laboratory.

        To secure uniformity of temperature throughout
the whole body of the water in the bath the water is
kept in constant circulation.   A lead pipe of 30 mm.

internal diameter lying on the bottom of the tank
extends from one end of the tank to the other, where it
joins a larger vertical brass pipe which extends
upwards to within a short distance from the surface of
the water.   By means of a small fan propellor placed
in the upper end of the brass pipe, the water is
constantly drawn into the lead pipe at the bottom of
the tank at one end and delivered at the surface of the
water at the other end.   The propellor is rotated by
means of friction gearing driven by a small motor.   By
this means so uniform a temperature is maintained in
the water that differences cannot be detected on ther-
mometers graduated to $0^{0}.1$.

        To keep the air in the space above the water
at a uniform temperature and as nearly as possible
equal to that of the water, a similar device is used.
Two lead pipes of the same size as that through which
the water is pumped, one on either side of the tank,
extend from the top of the enclosed space downward
through the water and along the bottom of the tank to
the opposite end, where they meet and connect with a
larger vertical brass pipe, which in turn reaches just

above the surface of the water.   By means of a
rotating fan the warmer air in the upper part of the
house is constantly drawn through the pipes and
delivered at the other end of the tank above the surface
of the water.   The machinery by which the pump and
fan are propelled is located entirely outside the house
so that the heat generated does not sensibly affect the
temperature of the bath.

Fig. 3 is a photograph of the bath together
with a number of other pieces of apparatus used in the
work.   Designated by d is the top of the bath stripped
of its upholstery; e is the glass window without its
curtains; f is the cathetometer; while within the bath
are seen parts of the vertical portions of the air
pipes (i and h).   Within the bath are also seen three
iron plates resting upon the edges of the tank and
serving to hold in place the galvanized iron cans (a
Fig. 3,),in one of which the cell is placed while a
measurement is in progress.   The cans are weighted
down by means of heavy cast iron cylinders (b Fig. 3).

In Fig. 4 are seen the can a, the cylinder b,
and the bottle c containing the cell, with which is
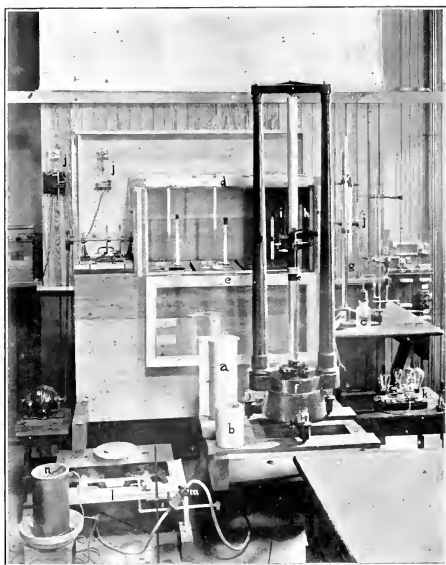
Fig. 3.
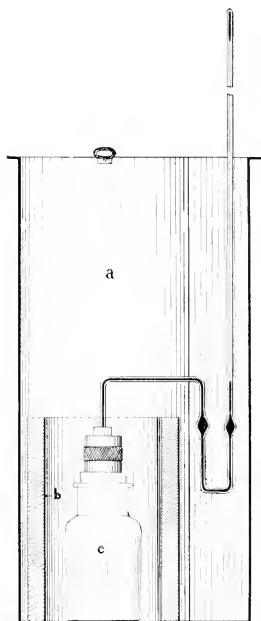
Fig. 4.

connected the manometer, in their respective positions
during a measurement.

During the progress of a measurement the open
end of the can containing the cell is covered closely
with a flannel pad of hair, so that the cell located
at a considerable depth below the surface of the water
shall acquire the temperature of the water, while the
enclosed air of the manometer takes on the temperature
of the surrounding air.

The thermometers used are graduated to $0.^{0}2$,
and were carefully compared with a thermometer tested
at the Reichsanstalt.

On account of the fact that the laboratory
building is heated only during working hours, the
variations of temperature outside the bath were very
large during the winter months, the lowest temperatures
being reached at night. Hence it was found necessary
to adopt means of securing more uniform temperature
conditions in the room in which the bath is located,
and thus avoid the effect of temperature variation on
the water and in the bath. The bath was enclosed by

a framework covered on both sides with thick muslin sized with gelatin to render it less pervious to air. The enclosure was provided with doors and windows of the same construction. The space thus enclosed has a length of 7. 3 meters, a width of 2 meters, and a height of 2.6 meters. To maintain a nearly constant temperature during the night, use is made of an electric stove controlled through a relay by means of an electric thermostat. To aid this stove there is provided also a gas stove regulated by means of an electric gas regulator controlled by an electric thermostat. In Fig. 3 is shown the electric stove n; l is the gas stove, m the gas regulator, while i. j, j, are the thermostats.

The means above described have proved most efficient in eliminating the source of error previously designated as "thermometer effects."

THE DETERMINATION OF INVERSION.

Having shown how two of the three great sources

of error have been eliminated, it remains to consider
the means that have been taken to deal with the third,
the inversion of the cane-sugar in the cell during a
measurement of pressure.   The determinations of
inversion last year by means of Fehling's solution
gave results of a very dubious character, and there
was reason to believe that the inversion was considera-
bly greater than it was apparently found to be by the
method employed.

        It was then proposed to make use of the
polariscope in determining the inversion that takes
place in the cell, and it was very desirable to make
the determination by simply comparing the rotation of
a reserved portion of the solution whose pressure was
measured with the rotation of the solution removed from
the cell at the completion of the experiment.

        The procedure employed to bring about this much
desired end is described at some length in what follows.
It should be stated at the outset that all our solutions
whose pressure have been measured are made by dissolving
a gram-molecular wieght of sugar, or proportional part
of the same, in 1000 grams of water, all weights being

corrected for air displacement.   These solutions
are designated as "weight-normal," etc.   Further, as
the basis of our calculations, the atomic weight of
hydrogen is taken as unity.

The Saccharimeter.-

        The instrument used in this work is the Schmidt
and Haensch   half-shade saccharimeter with triple
field and double quartz-wedge compensation.   The
instrument is so mounted as to insure the greatest
stability and rigidity, and the pinion for moving the
wedges is lengthened so that the observer can move it
with his hand resting on the table, a small detail that
adds much to the comfort of manipulation.   In this
instrument a small six-volt incandescent lamp of Haensch
and Schmidt is employed.   This lamp enclosed in the
polarized end of the saccharimeter affords a light of
greater intensity than the sodium flame, with very
little heating effect.   To cut off objectionable rays

        For detailed description, see Schmidt and Haensch:
Beschreibung und Gebrauchs-anweisung zu den Polar-
isations - Apparaten (1896), and their Spezial -
Preisliste (1902).

and obtain a uniform field there is placed between the
source of light and the polarizer an absorption cell of
potassium bichromate solution.   The end point is
determined by equality of shade.

The scale of the instrument is the Ventzke-
Soleil.   One hundred degrees on this scale correspond
to $34^{o}.55$ (D ray), and $39^{o}.10$ (j ray), on the circular
scale.   Accompanying the scale is a vernier with which
readings can be made to one-tenth of a degree.   The
"normal solution" for this instrument is one containing
26.048 grams of cane-sugar, weighed in air with brass
weights, in 100 Mohr cubic centimeters at $17^{o}.5$.   Such
a solution polarized in a two-decimeter tube produces
a rotation of exactly 100°.

Application of the Saccharimeter to the
Determination of Inversion.-

The application of the saccharimeter to the
determination of the inversion that takes place in a
solution during a measurement of osmotic pressure, by
simply observing the difference between the rotation
of a reserved portion of the solution and the rotation

of the solution after the experiment, was made possible
by the following considerations.

In the above standard solution, 26.048 grams
of sugar are weighed in air with brass weights.   This
weight corrected for air displacement = 26.064 grams.
Since 100 Lohr cubic centimeters = 100.23 $\underline{true}$ cubic
centimeters, the standard solution contains 26.064
grams of sugar in 100 $\underline{true}$ cubic centimeters.   Further,
100 $\underline{true}$ centimeters = 100.28 cc. at 20°.   Therefore,
a solution of 26.077 grams of sugar in 100 cc. of
solution at 20°, made up in a flask calibrated for 20°,
would produce a rotation of 100° when polarized in a
two-decimeter tube, or 1° rotation would correspond to
0.26077 gram in 100 cc.   This solution contains 23.68
per cent. of sugar.   A 0.9 weight-normal solution is
a 23.41 per cent. solution.   Since the specific
rotatory power of cane sugar does not change appreciably
with even greater differences in concentration, the
same value, 66.52, is taken for the "standard solution"
and the 0.9 normal solution.   This value was calculated

from Tollens' formula,

$$[\alpha]_D^{20} = 66.386 + 0.015035 \, p - 0.0003986 p^2,$$

where p = percentage of sugar.

Hence, in a 0.9 weight-normal solution of cane-sugar,
each degree of rotation corresponds to 0.26077 gram
in 100 cc., when polarized at 20° in a two-decimeter
tube.

The specific rotatory power of invert-sugar
was derived from Gubbe's formula,

$$[\alpha]_D^{20} = -19.657 - 0.0361 \, c,$$ where c = number
of grams invert-sugar in 100 cc. C was taken equal
to 0.1 and 1.0, these values being the extremes of the
concentrations of invert-sugar with which we have had
to deal. The value of for these two extremes is
-19.67.

Ber. d. chem. Ges. 10. 1403 (1877); Landolt,
Optische Drehungsvermögen.

Ber. d. chem. Ges. 18, 2207; Z. V. Rbz. - ind.
1884, 1315, Landolt, Optische Drehungsvermögen.

The ratio of the specific rotatory power of
invert-sugar to that above for cane-sugar is 0.2957. or
1 gram of invert-sugar produces the same rotation, in
opposite direction. that 0.2957 gram of cane-sugar
produces.   If 0.26077 gram of cane-sugar is inverted
there will be formed 0.27450 gram of invert-sugar.
Multiplying 0.27450 by 0.2957 we obtain 0.081169, the
quantity of cane-sugar which is equivalent in rotating
power to 0.27450 gram of invert-sugar.   This quantity
of cane-sugar would produce a rotation of $0°.311$, or
0.27450 gram of invert-sugar causes a laevo rotation
of $0°.311$.

Consequently. if 0.26077 gram of cane-sugar
is inverted in 100 cc. of a 0.9 weight-normal solution,
there will be a loss of $1°$ in rotation due to the loss
of 0.26077 gram of cane-sugar.   The 0.27450 gram of
invert-sugar formed will produce a further loss of
$0°.311$.   The total loss, $1°.311$, corresponds to the
presence of 0.27450 gram of invert-sugar, or $1°$ loss
=0.20933 gram invert-sugar in 100 cc. of solution.

By applying the same line of reasoning to other

concentrations, results are obtained, which are given
in Table II.

From this Table it will be seen that the effect
of differences in concentration such as we have in the
solutions in question is very small indeed. The
average of the values in Column VIII. is 0.26084. For
a 0.1 weight-normal solution the value is 0.26112, a
difference from the average of 0.00028. This is the
greatest variation from the average, corresponding to
a rotation of 0°.001. This rotation is far less than
can be detected on our saccharimeter. The variation
from the average value of XII. is of a still less order.
Hence we feel justified in neglecting the slight effect
of differences in concentration. For our purposes the
averages of the values in Table II. are sufficiently
accurate.

The values in Table II. hold only for the
temperature of 20°. It now remains to consider the
effect of changes of temperature. The procedure is
essentially the same as above. The specific rotatory
power of cane-sugar at different temperatures is

calculated from the formula,

$$(\alpha)_D^t = (\alpha)_D^{20} - 0.0144 (t - 20).$$

Values for the specific rotatory power of invert-sugar are obtained from the formula of Gubbe,

$$(\alpha)_D^t = (\alpha)_D^{20} + 0.3041 (t - 20) + 0.00165 (t-20)^2 .$$

Table III. contains the results for six different temperatures including 20°.

Column VIII. of Table III. contains the quantities of invert-sugar in 100 cc. which correspond to a loss of 1° in rotation. In order, therefore, to determine the quantity of invert-sugar in every 1000 grams of water in any given solution of cane-sugar, which causes a loss of 1° in rotation, the value in Column VIII. must be multiplied by one-tenth the volume of the given solution.

In Table IV. will be found the specific gravities and volumes of ten weight-normal solutions. The

Landolt, Optische Drehungsvermogen, p. 531.

Ibid., p. 526.

TABLE II.

I.	II.	III.	IV.	V.	VI.
Weight normality.	Grams cane-sugar in 1000 grams of water.	Percentage concentration.	$(\kappa)_D^{20}$ for cane-sugar.	Grams invert-sugar in 100 cc. of solution.	$(\kappa)_D^{20}$ for invert-sugar.
0.10	33.96	3.284	66.431	0.10–1.00	–19.67
0.20	67.92	6.360	66.466	"	"
0.30	101.88	9.246	66.491	"	"
0.40	135.84	11.959	66.508	"	"
0.50	169.80	14.515	66.520	"	"
0.60	203.76	16.927	66.526	"	"
0.70	237.72	19.206	66.528	"	"
0.80	271.68	21.364	66.525	"	"
0.90	305.64	23.409	66.520	"	"
1.00	339.60	25.351	66.510	"	"

VII.	VIII.	IX.	X.	XI.	XII.
Ratio of VI. to IV.	Grams cane-sugar in 100 cc. producing 1° rotation.	Grams invert sugar formed from VIII.	Laevo rotation of IX.	Total loss in rotation.	Grams invert sugar in 100 cc. = 1° loss in rotation.
0.2961	0.26112	0.27487	0.3117	1.3117	0.20955
0.2959	.26098	.27472	.3115	1.3115	.20947
0.2958	.26088	.27461	.3114	1.3114	.20940
0.2958	.26081	.27454	.3113	1.3113	.20937
0.2957	.26077	.27450	.3113	1.3113	.20933
0.2957	.26075	.27447	.3113	1.3113	.20931
0.2957	.26073	.27445	.3113	1.3113	.20930
0.2957	.26075	.27447	.3113	1.3113	.20931
0.2957	.26077	.27450	.3113	1.3113	.20933
0.2957	.26080	.27453	.3113	1.3113	.20936

TABLE III.

Temperature.	I. $(\kappa)_D^t$ for cane-sugar.	II. $(\kappa)_D^t$ for invert-sugar.	III. Ratio of II. to I.	IV. Grams cane-sugar in 100 cc. = 1° rotation.
18°	66.53	− 20.37	0.3047	0.26072
19°	66.51	− 19.97	0.3003	0.26080
20°	66.50	− 19.67	0.2958	0.26084
21°	66.49	− 19.36	0.2912	0.26088
22°	66.47	− 19.06	0.2867	0.26096
23°	66.46	− 18.74	0.2820	0.26100

Temperature.	V. Grams invert-sugar formed from IV.	VI. Laevo rotation of V.	VII. Total loss in rotation.	VIII. Grams invert-sugar in 100 cc. = 1° loss in rotation.
18°	0.27445	$0^o.3207$	$1^o.3207$	0.20780
19°	0.27453	$0^o.3160$	$1^o.3160$	0.20861
20°	0.27457	$0^o.3114$	$1^o.3114$	0.20937
21°	0.27462	$0^o.3065$	$1^o.3065$	0.21019
22°	0.27470	$0^o.3018$	$1^o.3018$	0.21102
23°	0.27474	$0^o.2968$	$1^o.2968$	0.21186

TABLE IV.

Weight-Normal Solutions of Cane-Sugar.

Weight-normal concentration.	Grams of Sugar in 1000 grams of water.	Specific gravity at 20°.	Volume at 20°.
0.10	33.96	1.01283	1020.86
0.20	67.92	1.02515	1041.72
0.30	101.88	1.03697	1062.70
0.40	135.84	1.04814	1083.67
0.50	169.80	1.05900	1104.62
0.60	203.76	1.06942	1125.62
0.70	237.72	1.07947	1146.60
0.80	271.68	1.08906	1167.68
0.90	305.64	1.09833	1188.75
1.00	339.60	1.10728	1209.81

specific gravities were interpolated from the specific
gravities given by Morse and Frazer.

Table V. gives the quantity of invert-sugar in
1000 grams of water, which causes the loss of 1^{O} in
rotation at different temperatures.   The transition
here made from a volume to a weight basis is necessary
because the solutions whose osmotic pressure are
measured are made by dissolving the given weight of
sugar in 1000 grams of water.

It will be observed that in the values given
in Table V. no account is taken of the changes in
volume that occur at any other temperature than 20°.
By calculation we have found that for the given temper-
atures such omission does not affect the second decimal
place.   For this reason, and for the further reason
that we do not have at hand satisfactory data for making
these slight corrections, we have used the volume at
20° as the volume at all temperatures between 18° and
23°, and tabulated the results to only two decimal
places.

TABLE V. - Invert-Sugar in Grams per 1,000 Grams of

Water producing a Loss of 1° in Rotation.

Weight-Normal-Concen-tration.	18°	19°	20°	21°	22°	23°
0.10	2.12	2.13	2.14	2.15	2.15	2.16
0.20	2.16	2.17	2.18	2.19	2.20	2.21
0.30	2.21	2.22	2.23	2.23	2.24	2.25
0.40	2.25	2.26	2.27	2.28	2.29	2.30
0.50	2.31	2.32	2.32	2.33	2.34	2.35
0.60	2.34	2.35	2.36	2.37	2.38	2.38
0.70	2.38	2.39	2.40	2.41	2.42	2.43
0.80	2.43	2.44	2.44	2.45	2.46	2.47
0.90	2.47	2.48	2.49	2.50	2.51	2.52
1.00	2.51	2.52	2.53	2.54	2.55	2.56

By the use of Table V. the correction for inversion in a pressure cell can be easily made. The rotation of the original solution and that of the solution removed from the cell after an experiment are determined in a two-decimeter tube. The loss in rotation in degrees multiplied by the value given in the table for the given concentration at the temperature of polarization gives the concentration of invert-sugar in grams per 1000 grams of water. The osmotic pressure that would be produced by one-half this quantity of invert-sugar is the correction that must be deducted from the observed osmotic pressure.

The accuracy of the above deductions was tested by a number of experiments. The method employed can best be shown by taking a particular experiment. All weights given are weights in a vacuum, and, unless otherwise stated, it is to be understood that polarizations were made in two-decimeter tubes.

A 0.10 weight-normal solution of cane-sugar containing 33.96 grams of sugar in 1000 grams of water gave a rotation, at 19°, of $12^\circ.73$. The volume of this solution at 20° was 1020.86 cc. A second solution

was then made containing 3.396 grams of sugar less per
1000 grams of water than the first solution. The
rotation at 19° was 11°.48. By interpolation from
volumes of Table IV. the volume of this solution was
found to be 1018.76 cc. at 20°. The rotation of the
latter solution was, therefore, greater than it would
have been had there been no change in volume due to the
difference of 3.396 grams of sugar. From the propor-
tion, 1018.76: 1020.86:: X : 11.48,

   X = 11.46, the rotation of 30.564 grams of cane-
sugar in 1020.86 cc. of solution.
12.73 − 11.46 = 1.27, which is the loss in rotation in
a 0.10 weight-normal solution due to loss of 3.396 grams
of sugar.

        3.396 grams of sugar were then inverted by
Clerget's method, the solution made up to 1000 cc.,
and polarized at 20 in a 4 - decimeter tube. The
laevo rotation was 0°.2. This value divided by 2 gives
the rotation of 3.5748 grams of invert-sugar in 1000
cc. of solution, at 20 , in a 2-decimeter tube. From
the proportion,

   1020.86 : 1000 :: 0.4 : X,

$\lambda = 0.59$, the rotation of 3.5748 grams of invert-sugar
in 1000.86 cc. of solution. Dividing 3.5748 by the
sum of 1.37 and 0.53, we obtain 2.15, the weight of
invert-sugar that must be present in a 0.1% weight-
volume solution of cane-sugar to cause a loss or 1°
in rotation. This value agrees very closely with the
value given in Table V.

In the remaining experiments the procedure was
the same as above, except that the inversion of 3.536
grams of cane-sugar was not repeated. The results of
all experiments are given in Table VI.

TABLE VI.

Column I.   – Weight-normality of the solution.
Column II. – Temperature of Rotation.
Column III.– Rotation of I.
Column IV. – Rotation of the solution containing
              3.396 grams less sugar per 1000
              grams water, corrected for differ-
              ence in volume.
Column V.   – Laevo rotation of 3.5748 grams
              invert-sugar in Solution I.
Column VI. – Grams of invert-sugar corresponding
              to loss of 1° rotation.

I.	II.	III.	IV.	V.	VI.
0.10	19°	12°.73	11°.46	0°.39	2.15
0.30	20°	36°.30	35°.03	0°.38	2.17
0.50	20°	58°.90	57°.61	0°.36	2.17
0.70	19°	78°.89	77°.70	0°.35	2.32
0.90	20°	98°.50	97°.31	0°.34	2.34
1.00	20°	107°.40	106°.37	0°.33	2.63

The data above presented afford an accurate and direct
method for determining inversion in all cases where
loss in rotation can be attributed solely to inversion.
There has been observed, in general, in our solutions,
a greater and greater loss in rotation as the concen-
tration of the solution increased, and tests by
Fehling's method revealed the fact that the inversion
in the cell was greater in the case of the more con-
centrated solutions.   The agreement here leaves little
room for doubt that the magnitude of the loss in
rotation is a true indication of the extent of the
inversion that has taken place.   There is no evidence
going to show that the rotatory power of cane-sugar is
affected by the pressure to which it has been subjected.
Such, however, could be considered a possibility.

     But there is one cause other than inversion
that can with certainty be stated as having an influence
on the magnitude of the loss in rotation, namely,
dilution of the solution during the experiment, and in
the application of the above method, this fact has not
been overlooked.   To what extent it has been possible
to take it into account, and in what way the attempt

has been made to distribute the loss in rotation between
inversion and dilution will be explained in connection
with a discussion of dilution.

THEORETICAL CONSIDERATIONS.

The view generally held regarding the relation
between the osmotic pressure of solutions and the
elastic pressure of gases seems to be that expressed
by Ostwald: "Dissolved substances exert the same
pressure, in the form of osmotic pressure, as they
would exert were they gasified, at the same temperature,
without change of volume."   Taking this view, the
osmotic pressures of concentrated solutions present
abnormalities, and the rule above set forth can apply
only to dilute solutions.

On the other hand, Morse and Frazer found that
when they dissolved a gram-molecular weight of cane-
sugar in 1000 grams of water, i. e., in that mass of
the solvent which has the unit volume at its temperature

of maximum density, the osmotic pressure of that
solution at 20° was in close accord with the pressure
of a gram-molecular weight of hydrogen confined, at
the same temperature, in the space of 1 litre (volume
of unit mass of solvent at temperature of greatest
density).   To repeat, "Cane-sugar, dissolved in water,
exerts an osmotic pressure equal to that which it would
exert if it were gasified at the same temperature and
the volume of the gas were reduced to that of the
solvent in the pure state."

Accepting the latter view as the correct one,
all the solutions whose osmotic pressures are recorded
in this paper were prepared by dissolving a gram-mol-
ecular weight of cane-sugar, or a decimal part of the
same, in 1000 grams of water, all weights being correct-
ed for air displacement.   Taking the atomic weight of
hydrogen as 1.00, the molecular weight of cane-sugar
becomes 3396.   The various solutions are designated
as weight-normal, etc., to distinguish them from
solutions made up on the volume basis.

The sugar used was the purest obtainable "rock

candy," whose purity was carefully tested by the
optical method.   To every solution of sugar was added
0.0839 gram of potassium ferrocyanide per 100 grams of
water, while to the water outside of the cell was added
0.1239 gram of copper sulphate per 100 grams of water,
these quantities being considered as isotonic equiva-
lents.   The object of so doing was to provide for the
mending of any ruptures occurring in the membrane during
the progress of an experiment, and also to diminish
the slight tendency of the membrane to dissolve in the
solution.

　　The value given by Morley for the weight of a
litre of hydrogen, under standard conditions of tem-
perature and pressure, at latitude 45°, is 0.089873 gram,
which corrected to the latitude of Baltimore becomes
0.089826 gram.   Dividing 2, the molecular weight of
hydrogen, by this value, 0.089826, we obtain 22.265,
the pressure of a gram-molecular weight of hydrogen
when its volume is reduced to 1 litre at 0°.

　　If, now, a gram-molecular weight of a substance,
dissolved in 1000 grams of water, exerts the same

pressure, as osmotic pressure, that a gram-molecular
weight of a gas exerts, as elastic pressure, when reduced
to a volume of a litre, and if osmotic pressure obeys
the law of Gay-Lussac, then the osmotic pressure of a
weight-normal solution, at 0°, is 22.265 atmospheres.
For temperature t, the value becomes 22.265 (1 + 0.00367 t),
or 22.265 + 0.0817 t atmospheres.

If P represents the osmotic pressure of any
solution at the temperature t, then $\dfrac{P}{22.265 + 0.0817 \, t}$
is the weight-normal concentration of the solution.
Therefore, $\dfrac{P}{22.265 + 0.0817 \, t}$: 1 :: W : M, or

$M = \dfrac{W}{P} (22.265 + 0.0817t)$, where W is the known weight
of the substance which exerts the osmotic pressure P,
and M is the molecular weight of the substance.

The molecular weights recorded in the last
column of the following tables (VII. - XVIII.) have
been calculated by means of this formula.

DISCUSSION OF CORRECTIONS.

"Membrane formers."- As above stated, 0.0839
gram of $K_4 F e (cn)_6 \cdot 3H_2 0$ per 100 grams of water is

atmospheres has been carefully considered.   On
account of the unsatisfactory and insufficient exper-
imental data to be obtained in this connection, and
further, on account of the fact that such deviation
must be small, and is part, at least, compensated by
a deviation in the law of Gay-Lussac, we have not
felt justified in attempting to make a correction for
this cause.

Adhering of enclosed air to walls of manometer. - As
the mercury rises in the manometer there must be some
air caught between the mercury and the walls of the
manometer, but we have no means of determining the
extent of the error due to this cause.

Expansion of glass. - The possible expansion of the
manometer tubing under pressure has been taken into
consideration.   Any such expansion would be expected
to manifest itself by a change in the length of the
ascending arm of the manometer. Under a pressure of 25
atmospheres the distance from the top of the manometer
to the lower scratch was found to be identical with
the distance between the same points when there was
no pressure being exerted.

Fermentation.- The fermentation of any of the products of inversion in the cell would affect the accuracy of the observations, but no evidence whatever has been obtained indicating any fermentation.

Leakage.- Careful examination of the outside solution after the experiment has shown no leakage of sugar through the membrane.

Dilution.- As stated in the consideration of the relation between loss in rotation and the inversion that has taken place in the cell, any dilution of the cell contents must be taken into account. Only when there is no dilution whatever is the loss in rotation of the solution an exact measure of the quantity of invert-sugar present.

The slight dilution due to the rise of the mercury in the manometer under pressure would not affect appreciably the rotation of the solution, owing to the fact that the total capacity of the largest manometer used is only 0.10 cc., and so much mechanical pressure is constantly brought to bear upon the cell contents and the mercury that the actual distance through which the mercury rises in consequence of the

...t of of water is really very small.   In the case of
the normal soluti ns where the effect of such dilution
would be greatest, the distance through which the mer-
cury rose after sufficient mechanical pressure had
been brought to bear to hold the stopper in place was
less than one-thirtieth the length of the original
air column.

Owing to the fact that the cell walls always
contain a little wat r, some dilution should normally
be expected from this cause.   To remove as far as
possible all water in the interior of the cell before
setting the cell up for a measurement of pressure, the
cell is always carefully rinsed out several times with
the solution whose pressure is to be determined.   But
during the time required for setting up the cell there
is necessarily a little dilution due to the attraction
of the water in the walls of the cell to the sugar of
the solution.   The extent of this dilution, and of any
further dilution that may be due to a slight compression
of the rubber stopper which is of course, or an expansion
of the cell, can not be determined.

The next smaller source of dilution is that
due to the slipping of the rubber stopper or of the

manometer upward through the stopper.   Attention has
already been called to the means tried to prevent both
of these sources of error, but, in spite of most care-
ful attention, in a number of experiments considerable
dilution has occurred from these causes.   It manifests
itself by a rise in the position of the top of the
manometer as determined repeatedly throughout an ex-
periment, and by a consequent excessive loss in the
rotation of the solution.   In _every_ case recorded,
where there has been observed any considerable rise in
the top of the manometer during an experiment, there
has been observed at the conclusion of the experiment
a larger loss in rotation than was observed in experi-
ments with the same solution where there was observed
no change in the position of the top of the manometer.
If in an experiment no change is observed in the posi-
tion of the top of the manometer, it is practically
certain no dilution has occurred from this cause.   But
even here the loss in rotation may be affected some
by the slight dilution due to the other causes above
mentioned.   The problem is manifestly a complicated one.

In the experiments recorded in the following

tables an attempt has been made to distribute the observed loss in rotation between inversion and dilution. The plan adopted can best be illustrated by a particular example.   Take the case of the two experiments with the 0.4 weight-normal solutions, Tables X. and XI. In Experiment 1, the rise in the manometer was 0.3 mm., the loss in rotation $0^{0}.8$. In Experiment 2, the rise of the manometer was 1.18 mm., and the loss in rotation was $1^{0}.3$.   In Experiment 1, the loss in rotation, $0^{0}.8$, is taken as a correction for inversion.   In Experiment 2, the same correction is applied for inversion, while $0^{0}.5$ ($1^{0}.3 - 0^{0}.8$) loss in rotation is applied as a correction in the opposite direction for dilution.

The same procedure is followed in the experiments with each of the other concentrations.   In the experiment where there has been observed the least rise in the position of the manometer, all loss in rotation is calculated as inversion, while in the other experiment or experiments where there has been observed a greater rise in the position of the manometer, the excess loss in rotation is calculated as dilution.

However, in making the corrections on this

basis, the author is not mindful of the fact that
even in the best experiments none of the loss in rota-
tion must be due, not to inversion, but to dilution.

RECORD OF EXPERIMENTS.

        In carrying out a measurement of osmotic
pressure, before setting away the cell and manometer
in their respective places in the bath, preliminary
readings are taken on the standard scale of the position
of the top of the manometer, the height of the mercury
in the manometer, the lower line of reference, scratch
No. 1, the position of the solution in the bulb on the
bend of the manometer, and the position of the surface
of the water in which the cell is placed.   The tem-
perature of the room and the barometric pressure are
also observed.

        These observations furnish all the data neces-
sary for calculating the pressure of liquids in the
cell and manometer, and also the initial pressure on
the enclosed air of the manometer.

After placing the cell and manometer in the
bath, during the further progress of the experiment,
it is necessary only to take readings of the temperature
of the water in the bath, the temperature of the air
around the manometer, the barometric pressure, and the
relative positions of the top of the manometer and
the top of the mercury column in the manometer.   The
barometric readings are corrected for temperature,
latitude and altitude.   As previously mentioned, all
observations of the length of air column in the manometer
are corrected for double meniscus, the meniscus of the
thread of mercury in the upper portion of the manometer
and that of the mercury column being regarded as
spherical.

Values used in Computations.

Temperature coefficient of gases	= 0.00367.
Coefficient of cubical expansion of mercury,	= 0.0001818.
Weight of 1 litre of hydrogen, at 0°, at Baltimore,	= 0.089826 gram.
Pressure of a gram-molecular weight of hydrogen, in 1 litre, at 0°,	=22.265 atmospheres.

0.20 Weight-Normal Solution - Experiments 1, 2, 3.

Sugar dissolved in 1000 grams of
        water,   =   67.92 grams.
Volume of solution at 20° = 1041.72 cc.
Concentration of solution ac-
        cording to volume-
        normal standard,   =   0.1920.

Experiment 1. --

      Rise of manometer   = 2.78 mm.
      Loss in rotation,   = $0^{\circ}.7$.
      Loss in rotation ascribed
         to inversion,   = $0^{\circ}.5$.
      Loss in rotation ascribed
         to dilution,   = $0^{\circ}.2$.

Experiment 2. -

      Rise in manometer,   = 1.44 mm.
      Loss in rotation,   = $0^{\circ}.7$.
      Loss in rotation ascribed
         to inversion,   = $0^{\circ}.5$.
      Loss in rotation ascribed
         to dilution,   = $0^{\circ}.2$.

Experiment 3. -

      Rise in manometer,   = 0.19 mm.
      Loss in rotation,   = $0^{\circ}.5$,
   all ascribed to inversion.

Table VII

SUBSTANCE

Original Wt. Normal Concentration of Solution

Rotation of Original Solution

Rotation at Conclusion of Experiment

Loss in Rotation

Calibration Units of Air in Manometer

Time of Setting up Cell

Experiment No.

Manometer Used No.

Capillary Depression

Cell Used

Resistance of Membrane

Initial Pressure

Time	Temperature		Volume of Air in Manometer		Corrections			Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Capillary Depression				

SUBSTANCE

Original Wt. Normal Concentration of Solution

Rotation of Original Solution

Rotation at Conclusion of Experiment

Loss in Rotation

Calibration Units of Air in Manometer

Time of Setting up Cell

Experiment No.

Manometer Used No.

Capillary Depression

Cell Used

Resistance of Membrane

Initial Pressure

TIME	TEMPERATURE		VOLUME OF AIR IN MANOMETER		CORRECTIONS				Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Temperature	Capillary Depression				

SUBSTANCE

Original Wt. Normal Concentration of Solution

Rotation of Original Solution

Rotation at Conclusion of Experiment

Loss in Rotation

Calibration Units of Air in Manometer

Time of Setting up Cell

Experiment No.

Manometer Used No.

Capillary Depression

Cell Used

Resistance of Membrane

Initial Pressure

TIME	TEMPERATURE		VOLUME OF AIR IN MANOMETER		CORRECTIONS					Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Inversion	Capillary Depression					

Comments.

Previous to Experiment 1, after the preparation
and development of the membrane already described, cell
G had been used for a measurement of the osmotic
pressure of a 0.6 weight-normal solution.   Up to the
time of Experiment 1, the cell had been subjected to
the membrane forming process, in all, 17 hours.

Attention is called to the rapidity with which,
in Experiment 3, the pressure reached a maximum.

When molecular weights are determined by
osmotic pressure, the accuracy of the results increases
with the concentration of the solution.   A mistake
of 0.10 of an atmosphere in the pressure of a 0.2
weight-normal solution produces an error of 7.08 units
in the estimated molecular weight of cane-sugar.

<u>0.4 Weight-Normal Solution – Experiments 1, 2.</u>

Sugar dissolved in 1000 grams of
    water,   = 135.84 grams.
Volume of solution at 20° = 1083.67 cc.
Concentration according to the
    <u>volume-normal standard</u>, =   0.3691.

<u>Experiment 1.</u> –

    Rise of manometer   = 0.30 mm.
    Loss in rotation   = $0.^{\circ}8$.
Loss in rotation all ascribed
       to inversion.

<u>Experiment 2.</u> –

    Rise of manometer   = 1.18 mm.
    Loss in rotation   = $1.^{\circ}3$.
Loss in rotation ascribed
       to inversion   = $0.^{\circ}8$.
Loss in rotation ascribed
       to dilution   = $0.^{\circ}5$.

<u>Comments.</u>

In these two experiments, the maximum pressure
was reached in 9 and 7 hours respectively.

Plate X

SUBSTANCE

Original Wt. Normal Concentration of Solution

Rotation of Original Solution

Rotation at Conclusion of Experiment

Loss in Rotation

Calibration Units of Air in Manometer

Time of Setting up Cell

Experiment No.

Manometer Used No.

Capillary Depression

Cell Used

Resistance of Membrane

Initial Pressure

TIME	TEMPERATURE		VOLUME OF AIR IN MANOMETER		CORRECTIONS				Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Inversion	Capillary Depression				

SUBSTANCE

Original Wt. Normal Concentration of Solution		Experiment No.
Rotation of Original Solution		Manometer Used No.
Rotation at Conclusion of Experiment		Capillary Depression
Loss in Rotation		Cell Used
Calibration Units of Air in Manometer		Resistance of Membrane
Time of Setting up Cell		Initial Pressure

TIME	TEMPERATURE		VOLUME OF AIR IN MANOMETER		CORRECTIONS			Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Capillary Depression				

<u>0.6 Weight-Normal Solution - Experiments 1, 2, 3.</u>

Sugar dissolved in 1000 grams
   of water   = 203.76 grams
Volume of solution at 20° = 1125.62 cc.
Concentration according to the
   <u>volume-normal</u> standard   =   0.5322.

<u>Experiment 1.</u> -

      Rise of manometer   =   3.78 mm.
      Loss in rotation   = $2.^{\circ}8.$
      Loss in rotation ascribed
         to inversion   = $1.^{\circ}8.$
      Loss in rotation ascribed
         to dilution   = $1.^{\circ}0.$

<u>Experiment 2.</u> -

      Rise of manometer   =   0.83 mm.
      Loss in rotation   = $1.^{\circ}9.$
      Loss in rotation all entered
         as an inversion cor-
         rection.

<u>Experiment 3.</u> -

      Rise of manometer   =   0.64 mm.
      Loss in rotation   = $1.^{\circ}8,$
         the whole ascribed to
         inversion.

<u>Comments.</u>

    In Experiment 2, the maximum pressure was

attained in 7 hours after the cell was set up.   In

the other two experiments, 1 and 3, a maximum had al-
most been reached in 7 and 11 hours respectively.

Attention is directed to constant temperature
of the solution maintained throughout these experiments.

SUBSTANCE

Original Wt. Normal Concentration of Solution
Rotation of Original Solution
Rotation at Conclusion of Experiment
Loss in Rotation
Calibration Units of Air in Manometer
Time of Setting up Cell

Experiment No.
Manometer Used No.
Capillary Depression
Cell Used
Resistance of Membrane
Initial Pressure

TIME	TEMPERATURE		VOLUME OF AIR IN MANOMETER		CORRECTIONS				Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Increase	Capillary Depression				

SUBSTANCE

Original Wt. Normal Concentration of Solution

Rotation of Original Solution

Rotation at Conclusion of Experiment

Loss in Rotation

Calibration Units of Air in Manometer

Time of Setting up Cell

Experiment No.

Manometer Used No.

Capillary Depression

Cell Used

Resistance of Membrane

Initial Pressure

TIME	TEMPERATURE		VOLUME OF AIR IN MANOMETER		CORRECTIONS					Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Inversion	Capillary Depression					

PLATE XII

SUBSTANCE C

Original Wt. Normal Concentration of Solution

Experiment No.

Rotation of Original Solution

Manometer Used No.

Rotation at Conclusion of Experiment

Capillary Depression

Loss in Rotation

Cell Used

Calibration Units of Air in Manometer

Resistance of Membrane

Time of Setting up Cell

Initial Pressure

TIME	TEMPERATURE		VOLUME OF AIR IN MANOMETER		CORRECTIONS				Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Inversion	Capillary Depression				

0.8 Weight–Normal Solution.–   Experiments 1, 2.

Sugar dissolved in 1000 grams
    of water   – 271.68 grams.
Volume of the solution at 20° –1167.68 cc.
Concentration according to the
    volume–normal standard   –   0.6834.

Experiment 1. –

       Rise of manometer   –   0.32 mm.
       Loss in rotation   – $3.^O2$.
       Loss in rotation ascribed
           to inversion   – $3.^O2$.

Experiment 2. –

       Rise of manometer   –   1.80 mm.
       Loss in rotation   – $3.^O9$.
       Loss in rotation ascribed
           to inversion   – $3.^O2$.
       Loss in rotation ascribed
           to dilution   – $0.^O7$.

Comments.

The maximum pressure was nearly attained in
less than five hours, in Experiment 1.   In these two
experiments there was practically no change of temper-
ature in the water of the bath.

Plate X

SUBSTANCE

Original Wt. Normal Concentration of Solution   Experiment No.

Rotation of Original Solution   Manometer Used No.

Rotation at Conclusion of Experiment   Capillary Depression

Loss in Rotation   Cell Used

Calibration Units of Air in Manometer   Resistance of Membrane

Time of Setting up Cell   Initial Pressure

TIME	TEMPERATURE		VOLUME OF AIR IN MANOMETER		CORRECTIONS				Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Inversion	Capillary Depression				

SUBSTANCE

SUBSTANCE

Original Wt. Normal Concentration of Solution

Rotation of Original Solution

Rotation at Conclusion of Experiment

Loss in Rotation

Calibration Units of Air in Manometer

Time of Setting up Cell

Experiment No.

Manometer Used No.

Capillary Depression

Cell Used

Resistance of Membrane

Initial Pressure.

TIME	TEMPERATURE		VOLUME OF AIR IN MANOMETER		CORRECTIONS				Osmotic Pressure, Corrected	Theoretical Gas-Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Immersion	Capillary Depression				

1.0 Weight-Normal Solution - Experiments 1, 2.

Sugar dissolved in 1000 grams of water	=	339.6 grams.
Volume of solution at 20°	=	1209.81 cc.
Concentration of the solution according to the volume-normal standard	=	0.8266.

Experiment 1. -

Rise of manometer	=	0.88 mm.
Loss in rotation	=	2.°4,
all ascribed to inversion.		

Experiment 2. -

Rise of manometer	=	2.97 mm.
Loss in rotation	=	4.°0.
Loss in rotation ascribed to inversion	=	2.°4.
Loss in rotation ascribed to dilution	=	1.°6.

Comments.

The cells used in these experiments were A and B which had been used last year by Morse and Frazer in their measurements of osmotic pressure, and this year for some time in the measurement of the osmotic pressure of grape-sugar solutions. It will be noted that about 59 hours were required for the maximum pressure to

develop.

      A mistake of 0.1 atmosphere in the osmotic pressure of a weight-normal solution produces an error of only 1.4 units in the estimated molecular weight of cane-sugar.

SUBSTANCE

Original Wt. Normal Concentration of Solution

Rotation of Original Solution

Rotation at Conclusion of Experiment

Loss in Rotation

Calibration Units of Air in Manometer

Time of Setting up Cell

Experiment No.

Manometer Used No.

Capillary Depression

Cell Used

Resistance of Membrane

Initial Pressure

TIME	TEMPERATURE		VOLUME OF AIR IN MANOMETER		CORRECTIONS					Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Inversion	Capillary Depression					

$\sim$ $\times$ $\textit{11}$.

SUBSTANCE

Original Wt. Normal Concentration of Solution   Experiment No.

Rotation of Original Solution   Manometer Used No.

Rotation at Conclusion of Experiment   Capillary Depression

Loss in Rotation   Cell Used

Calibration Units of Air in Manometer   Resistance of Membrane

Time of Setting up Cell   Initial Pressure.

TIME	TEMPERATURE		VOLUME OF AIR IN MANOMETER		CORRECTIONS			Osmotic Pressure, Corrected	Theoretical Gas Pressure	Difference between Pressure Found and Calculated	Mol. Wt. Calculated from Osmotic Pressure
	Solution	Air in Manometer	Uncorrected	Corrected	Atmospheric Pressure	Liquids in Manometer	Capillary Depression				

TABLE XIX.   —   Summary of Results.

Weight-normal concentration of solution.	Osmotic pressure, observed. (Atmospheres).	Gas pressure calculated for same temperature. (Atmospheres).	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weight. Mean values.
		Experiment 1.			
0.2	4.73	4.79	-0.06	343.93	
	4.73	4.79	-0.06	344.16	
	4.71	4.79	-0.08	345.76	
	4.71	4.80	-0.09	345.99	344.96
		Experiment 2.			
	4.81	4.80	+0.01	338.85	
	4.80	4.80	0.00	339.67	
	4.79	4.80	-0.01	340.38	
	4.76	4.80	-0.04	342.58	
	4.76	4.80	-0.04	343.09	340.90
		Experiment 3.			
	4.81	4.81	0.00	339.37	
	4.81	4.81	0.00	339.54	
	4.80	4.81	-0.01	340.31	339.74
		Experiment 1.			
0.4	9.62	9.61	0.01	339.17	
	9.64	9.61	0.03	338.61	
	9.64	9.61	0.03	338.72	
	9.65	9.61	0.04	338.43	338.73

Weight-normal concentration of solution.	Osmotic pressure, observed. (Atmospheres).	Gas pressure calculated for same temperature. (Atmospheres).	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weight. Mean values.
		Experiment 2.			
0.4	9.69	9.63	+0.06	337.44	
	9.69	9.63	+0.06	337.50	
	9.69	9.63	+0.06	337.55	337.50
		Experiment 1.			
0.6	14.70	14.55	+0.15	336.14	
	14.74	14.55	+0.19	335.35	
	14.76	14.55	+0.21	334.89	
	14.76	14.55	+0.21	334.89	335.32
		Experiment 2.			
	14.69	14.54	+0.15	336.20	
	14.70	14.55	+0.15	336.03	
	14.71	14.55	+0.16	335.90	
	14.70	14.55	+0.15	336.13	336.06
		Experiment 3.			
	14.74	14.54	+0.20	335.00	
	14.77	14.54	+0.23	334.32	
	14.79	14.54	+0.25	333.87	
	14.78	14.54	+0.24	334.10	
	14.77	14.54	+0.24	334.32	334.32

Weight-normal concentration of solution	Osmotic pressure, observed (Atmospheres)	Gas pressure calculated for same temperature. (Atmospheres)	Difference between pressure observed and calculated	Molecular weight calculated from observed pressure	Molecular weight. Mean values.

Experiment 1.

0.8	19.30	19.35	-0.05	340.53	
	19.36	19.35	-0.09	341.27	
	19.29	19.35	-0.06	340.73	
	19.33	19.35	-0.02	340.03	
	19.34	19.35	-0.01	339.85	340.48

Experiment 2.

	19.35	19.36	-0.01	339.79	
	19.31	19.36	-0.05	340.49	
	19.43	19.36	+0.07	338.39	
	19.44	19.36	+0.08	338.22	
	19.42	19.36	+0.06	338.51	339.08

Experiment 1.

I.0	24.47	24.19	+0.28	335.70	
	24.49	24.19	+0.30	335.45	335.57

Experiment 2.

	24.05	24.28	-0.23	342.78	
	24.05	24.28	-0.22	342.66	342.72

TABLE XX. - <u>Mean Molecular Weight for each Concentration.</u>

Concentration	Molecular weight.
0.2	341.87
0.4	338.12
0.6	335.23
0.8	339.73
1.0	339.15
Mean of all determinations	338.83
Theoretical..........	339.60
Difference,......	0.77

In the following Table XXI. is given a brief summary of the results obtained by Mr. W. L. Kennon in the measurement of the osmotic pressure of cane-sugar solutions of 0.1, 0.3, 0.5, 0.7, and 0.9 <u>weight-normal</u> concentrations.

TABLE XXI.

Weight-normal concentration of solution.	Osmotic pressure, observed. (Atmospheres).	Gas pressure calculated for same temperature. (Atmospheres).	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weight. Mean values.

Experiment 1.

0.1	2.50	2.41	+0.09	329.09	
	2.50	2.41	+0.09	329.14	
	2.52	2.42	+0.10	326.58	
	2.52	2.42	+0.10	326.58	327.85

Experiment 2.

	2.53	2.42	+0.11	325.40	
	2.56	2.42	+0.14	321.58	
	2.56	2.43	+0.13	321.63	
	2.56	2.43	+0.13	321.63	322.56

Experiment 1.

0.3	7.25	7.21	+0.04	337.68	
	7.23	7.21	+0.02	338.72	
	7.23	7.21	+0.02	338.72	338.37

Experiment 2.

	7.21	7.16	+0.05	337.36	
	7.21	7.16	+0.05	337.53	
	7.17	7.17	0.00	339.70	338.20

Weight-normal concentration of solution	Osmotic Pressure, observed. (Atmospheres)	Gas pressure calculated for same temperature. (Atmospheres)	Difference between pressure observed and calculated	Molecular weight calculated from observed pressure	Molecular weight. Mean values.
		Experiment 1.			
0.5	12.07	12.06	+ 0.01	339.29	
	12.06	12.05	+ 0.01	339.36	
	12.04	12.06	− 0.02	340.16	339.60
		Experiment 2.			
	12.19	12.10	+ 0.09	337.11	
	12.25	12.10	+ 0.15	335.46	
	12.23	12.10	+ 0.13	336.01	336.19
		Experiment 1.			
0.7	16.99	16.92	+ 0.07	338.39	
	16.94	16.92	+ 0.02	339.39	
	16.96	16.95	+ 0.01	339.40	
	16.92	16.96	− 0.04	340.37	339.39
		Experiment 2.			
	16.98	16.89	+ 0.09	338.87	
	16.96	16.89	+ 0.07	339.27	
	16.97	16.95	+ 0.02	339.14	
	16.92	16.98	− 0.06	340.70	339.49
		Experiment 1.			
0.9	21.90	21.87	+ 0.03	339.12	
	21.97	21.87	+ 0.10	338.04	338.58
		Experiment 2.			
	21.98	21.87	+ 0.11	337.89	
	22.05	21.87	+ 0.18	336.82	337.35

Mean of all determinations 335.75

CONCLUSIONS.

The results recorded in the foregoing pages of this paper strengthen the conclusion of Morse and Frazer that the determining factor in osmotic pressure is the numerical relation existing between the molecules of the dissolved substance and of the solvent, rather than the number of molecules of the dissolved substance contained in unit volume of the solution. Taking as the standard quantity of the solvent that mass of pure water which has the gas-unit volume, no abnormalities have to be accounted for in the case of the osmotic pressure of solutions of cane-sugar. On this basis the osmotic pressure of these solutions obeys the gas laws.

The margin of experimental error is still too great to admit of determining whether the correct standard is the volume of the solvent at the temperature of maximum density, or at the temperature at which the pressure is measured.

It is highly probable that, on this "weight-normal" basis, as in the case of the osmotic pressure of cane-sugar solutions, the osmotic pressures of most undissociated substances will be found to be in close accord with the hypothesis of Van't Hoff.

II.   THE SEMIPERMEABLE MEMBRANE OF COPPER

COBALTICYANIDE.

INTRODUCTION.

Since the discovery, in 1901, of Morse and
Horn   that the membrane of copper ferrocyanide could
be deposited more successfully and to better advantage
electrolytically than by the diffusion method of
Pfeffer, no less than twenty-six different precipitates
have been examined as to their osmotic activity, with
a view to determining which of them might be used to
advantage in cases where copper ferrocyanide could not
be used for one reason or another.

While quite a number of membranes studied
seemed to give promise of being thus useful, as judged

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simply by pressure measurements with open manometers,
or by the rate of overflow of the cell contents under
little more than one atmosphere pressure, no conclu-
sions could be drawn definitely as to what would be
their conduct were it attempted to use them in the
direct measurement of pressure with closed manometers.
The latter attempt was not made because of the great
difficulty of securing porous cups of unquestionable
character, whose walls could be counted upon to give
proper support to the membrane.   Any conclusions as to
the efficiency of a membrane based on results with cells
of questionable character must necessarily be of very
little value.   In this connection it should be noted
that many failures to make direct measurements of
osmotic pressure have been due, not to the membrane,
but to the faulty character of the cell wall in which
or upon which the membrane was deposited.   The im-
portance of keeping this distinction clearly in mind
can not be urged too strongly, for many conclusions
reached concerning osmotic pressure and its measurement
may be entirely erroneous for no other reason than
that the cell wall did not provide sufficient support
for the membrane.

been made in the solution of the problem of the porous
cup, and it has been found possible to provide a
number of very excellent cells.   It was suggested by
Professor Morse that the membrane of copper cobalticy-
anide be further studied by an attempt to use it in the
actual measurement of osmotic pressure.   An account
of the beginning that has been made in this direction
will be given in the following pages of this paper.

T H E   C E L L   U S E D.

The cell used in this work will be known as
Cell L. Before burning it had a length of 9.40 cm.,
an internal diameter at the open end of 2.49 cm., and
an external diameter just below the rim of 3.54 cm.
Previous to this work the cell had been used in several
experiments with zinc ferrocyanide, after which the
cell and its parts were all taken apart, the cement
entirely removed, and the membrane dissolved in potassium
hydroxide, the last traces being removed by electrolysis.
Afterwards the electrolysis was continued until no

alkali remained in the walls of the cell.   The parts
of the cell were then reassembled, it being necessary
to provide new parts.   The probable effect of the
treatment of the cell in this manner on the results of
later experiments will be considered further on,   It
will be unnecessary to describe the apparatus for the
removal of air from the cell walls, and that used in
the deposition of the membrane.   The apparatus and
method are identical with those previously described.
Cell L was of very fine texture as indicated by the low
rate of endosmose when a voltage of 100 was used, with
0.005 normal lithium sulphate solution as electrolyte.
It amounted on the average to about 15 cc. per hour.
In the deposition of the membrane 0.1 normal potassium
cobalticyanide solution was used inside the cell, while
a solution of the same concentration of copper sulphate
was placed outside.   The solution of potassium
cobalticyanide was always slightly acidified with acetic
acid to neutralize the effect of alkali, care being
taken to add the same quantity of acid each time so that
the magnitude of the resistance in the circuit during
the membrane deposition should not vary on account of

the presence of varying quantities of acid. The
solution in the cell was renewed every few minutes.

THE EXPERIMENTS

Preliminary experiments were made with another
cell to test the activity of the membrane. The
"overflow" method indicated considerable activity.

In view of the uncertainty as to what current
pressure was best suited to the deposition of the
membrane it was deemed advisable to make the first ex-
periments with a comparatively low voltage – 37 volts.

Accordingly, the membrane deposition was begun
as shown in the following record:

Record.

January 20, 1906.

Time.	Current.	Voltage.	Resistance.
3:00 P.M.	0.0050	37.6	7520
3:02 "	0.0080	37.6	4700
3:05 "	0.0044	37.6	8545
3:10 "	0.0034	37.6	11059
3:20 "	0.0026	37.6	14461
3:30 "	0.0022	37.6	17086
3:40 "	0.0020	37.6	18800
3:50 "	0.0019	37.6	19789
4:00 "	0.0019	37.6	19789
4:10 "	0.0018	37.6	20888
4:30 "	0.0018	37.6	20888
4:40 "	0.0016	37.6	23500
4:50 "	0.0016	37.6	23500
5:00 "	0.0016	37.6	23500

The cell was then taken down and placed in distilled water until February 1, when the deposition was continued.

Record.

February 1, 1906.

Time.	Current.	Voltage.	Resistance.
2:40 P.M.	0.0022	37.6	17090
2:45 "	0.0018	37.6	20888
2:50 "	0.0014	37.6	26857
3:00 "	0.0013	37.5	28846
3:10 "	0.0012	37.6	31333
3:20 "	0.0011	37.6	34181
3:30 "	0.0010	37.6	37600
3:40 "	0.0010	37.6	37600
3:50 "	0.0010	37.6	37600
4:00 "	0.0010	37.4	37400
4:10 "	0.0010	37.6	37600
4:20 "	0.0010	37.5	37500
4:30 "	0.0010	37.5	37500
4:40 "	0.0010	37.5	37500

Record.

February 2, 1906.

Time.	Current.	Voltage.	Resistance.
3:50 P.M.	0.0120	37.5	3125
3:55 "	0.0018	37.5	20833
—	—	—	—
3:50 P.M.	0.0010	37.5	37500
4:00 "	0.0010	37.5	37500
4:10 "	0.0010	37.5	37500
4:20 "	0.0010	37.5	37500
4:30 "	0.0010	37.5	37500

The above records are given in detail as

showing how uniformly the resistance increased until a
maximum was reached, and the behavior which would lead
one to expect good results in an attempt to make a
measurement with the membrane.

Experiment I.

In accordance with the usual procedure the cell
was set up with a preliminary solution of sugar. A
0.5 weight-normal solution made 0.1 normal with
potassium cobalticyanide was used. After attaching
the manometer to the cell in the usual way, the cell
was placed in a 0.1 normal solution of copper sulphate.
An initial mechanical pressure of about 1 atmosphere
was brought to bear on the cell contents and the
mercury in the manometer. The mercury immediately
began to fall. Mechanical pressure was again
brought to bear, but the mercury again fell, and never
showed any tendency to rise. However, such behavior
might be expected in a first experiment. The cell was
then taken down and placed in distilled water until
it was again desired to repeat the membrane forming
process.

Record.

On three following days the deposition was continued for four and one-half hours at the same voltage. At the end of this time the resistance of the membrane had reached 62100 ohms.

Experiment II.

The cell was again set up with the preliminary solution of sugar. The initial mechanical pressure was about 1 atmosphere. The mercury fell as in the previous experiment and showed no tendency whatever to rise.

On three more consecutive days, in all 5 1/2 hours, the membrane was reenforced. At the beginning, with a voltage of 37, the resistance of the membrane was only 8000 ohms, clearly showing it had been considerably ruptured in the last experiment. The record for the third day follows.

<center>Record.</center>

<center>February 9, 1906.</center>

Time.	Current.	Voltage.	Resistance.
2:50 P.M.	0.0010	37.6	37600
3:00 "	0.0006	37.8	63000
3:10 "	0.0004	37.8	94500
3:20 "	0.0004	37.8	94500
3:30 "	0.0004	37.8	94500
3:40 "	0.0003	37.8	126000
3:50 "	0.0003	37.8	126000
4:00 "	0.0003	37.7	125000
4:10 "	0.0003	37.7	125666
4:20 "	0.0003	37.7	125666
4:30 "	0.0003	37.7	125666
4:40 "	0.0003	37.7	125666

The high resistance here reached was taken as
an indication of a very satisfactory condition of
membrane. This has seemed to be the meaning of high
resistance in the case of the copper ferrocyanide
membrane.

<center>Experiment III.</center>

The cell was again set up with 0.5 normal cane-
sugar, and 0.1 normal membrane formers. Mechanical
pressure was repeatedly brought to bear, which was
followed in every case by a fall in the mercury. The mer-
cury never rose.The next day the cell was taken down

and set to soak in distilled water.

It was then decided to use a lower voltage for the deposition of the membrane to determine if better results could be obtained.

Record.

February 13, 1906.

Time.	Current.	Voltage.	Resistance.
3:40 P.M.	0.0008	11.6	14500
3:50 "	0.0004	11.6	29000
4:00 "	0.0003	11.6	38666
4:10 "	0.0002	11.6	58000
4:20 "	0.0001	11.6	116000
4:30 "	0.0001	11.6	116000
4:40 "	0.0001	11.6	116000
4:50 "	0.0001	11.6	116000

The deposition was continued after this, on three days, for 5 hours. At the end of this time the resistance was less than in the above record, namely, 38666 ohms. However, the cell was again set up with the usual solution.

Experiment IV.

The nut was screwed down on the stopper until there was an initial pressure of about 1.5 atmospheres.

It then rose about 15 mm.   The nut was again screwed down, after which the mercury began to fall and showed no tendency again to rise.

The remaining experiments were made using a voltage of about 112 for the deposition of the membrane, it being thought that possibly a higher voltage than previously used was required, and that better results would possibly be obtained.

Record.

February 20, 1906.

Time.	Current.	Voltage.	Resistance.
3:40 P.M	0.0082	112.3	13695
3:45 "	0.0033	112.2	34000
3:55 "	0.0022	112.2	51000
4:05 "	0.0019	112.1	59000
4:15 "	0.0017	111.5	65588
4:25 "	0.0016	111.5	69688
4:35 "	0.0015	111.0	74666

Record.

February 21, 1906.

Time.	Current.	Voltage.	Resistance.
3:05 P.M.	0.0047	112	23830
3:10 "	0.0035	112	32000
3:20 "	0.0031	112	36130
3:30 "	0.0030	112	37333
3:40 "	0.0027	112	41481
3:50 "	0.0026	112	43077
4:00 "	0.0022	112	50910
4:10 "	0.0024	112	46888

These records were not what one would consider promising, but the cell was again set up with the usual solutions.

Experiment V.

The behavior of the membrane was as in Experiment IV. There was at one time during the experiment a rise of mercury of about 8 m.., which could easily be accounted for by temperature change.

Record.

On February 22, the membrane deposition was resumed for about 1 1/2 hours. The resistance rose from 41400 to 111100 ohms. Voltage, 111.7.

February 23: Time of deposition = 2 hours.

Initial resistance = 32400 ohms.

Final resistance = 80000 ohms.

Experiment VI.

The cell was then set up again after the usual manner. An initial pressure of about 0.5 of an atmosphere was brought to bear. The mercury fell for

about 15 minutes, 10 mm.   It then began to rise until
in 35 minutes it was rising 1 mm. per minute.   In
three hours it rose 107 mm., equivalent to a pressure
of 1.5 atmospheres.   The theoretical pressure of the
solution was about 12 atmospheres.   The nut was then
screwed down on the stopper until there was a pressure
in the manometer of 2.5 atmospheres.   The mercury at
once began to fall and never afterwards rose again.

                    C O N C L U S I O N S.

        The above brief study would appear to show that
of the three different voltages employed for the deposi-
tion of the membrane, that of 37 volts was the most
satisfactory.   A maximum resistance of more than 125000
ohms was attained with this voltage.   With 12 volts a
nearly as good result was obtained, only in this case
the current was so small that very little membrane could
be deposited without devoting a great deal of time to
the deposition.   With the voltage of 37 there was a

regularity in the increase of the resistance, and the
maximum resistance was well maintained.   There would
seem to have been formed a fairly compact and evenly
distributed membrane.

On the other hand it would appear that a current
pressure of 110 volts was too high, and that the rapid
endosmose of water through the cell wall and membrane
was constantly tearing away the membrane, and consequent-
ly a constant resistance could not be maintained.

If the resistance developed in the deposition
of a membrane is resistance to endosmose, then we should
expect a greater resistance in the less porous cell.
Experience in this laboratory has shown that in the
very porous cells there is low resistance in the
deposition of the membrane, while the resistance becomes
greater according as the cell is less porous.   Now, if
the membrane is successfully deposited, it must cause
still greater resistance to endosmose, and if a very
high resistance is obtained, it can be taken as a pretty
certain indication of the satisfactory condition of the
membrane.

If the membrane is strong enough to resist the
effects of endosmose, then we should expect the resist-

ance to increase with time, and finally a resistance
to be reached which would be maintained constant for a
long time.   Any further increase in resistance would
be very slow on account of the now small additional
membrane deposited by the diminished current.   If
through any cause there should be injury done the
membrane, the resistance would decrease.   There is
probably a voltage at which the endosemose can just be
withstood by a given membrane without injury.   Past
experience in the laboratory has shown that the voltage
of 110 is best adapted to the deposition of the copper
ferrocyanide membrane, and that good results are not
obtained with a much higher voltage.   To determine at
what voltage the best results can be obtained in the
deposition of any other membrane, the problem must be
taken up systematically, and some considerable time
devoted to it.

That the membrane of copper cobalticyanide is
easily injured would seem to be confirmed by the behavior
observed in the above experiments.   The effect of
bringing to bear mechanical pressure on the contents of
the cell seems to be injurious.   In Experiment VI., a

rapid rise of the mercury was observed at the start,
but as soon as the nut was screwed down on the stopper,
the mercury fell.   Subsequent behavior of the membrane
upon being again subjected to the membrane forming
process would seem to render this view quite probable.
If the membrane be as weak as the above experiments
indicate, it can, of course, be of no service in the
direct measurement of osmotic pressure.

However, there remains one consideration that
makes it extremely doubtful as to how much importance
should be attached to the results of the above experi-
ments.   After these experiments had been made, it was
decided to remove the cobalticyanide membrane from the
cell and replace it by a membrane of copper ferrocyanide,
it being desired to use the cell in the exact measure-
ment of the osmotic pressure of cane-sugar solutions.
Accordingly the membrane of copper cobalticyanide was
dissolved in ammonia, and the cell afterwards prepared
for the deposition of the copper ferrocyanide.   But
all attempts to secure satisfactory results with the
latter membrane in this cell also failed.   The cell
was set up repeatedly with the preliminary half-normal
sugar solution, but never was a pressure of more than

five atmospheres attained.   This failure was probably
due to the previous use of the cell with the copper
cobalticyanide membrane, and the removal of this
membrane as described.   This explanation necessarily
brings up the question whether the failure to obtain
good results with the copper cobalticyanide was not
due to the previous use of the cell with the membrane
of zinc ferrocyanide.   Other attempts made in this
laboratory to remove a membrane from a cell and after-
wards obtain satisfactory results with the cell have
also failed.

These facts serve to emphasize the importance
of exercising the greatest care in the selection of the
cell in which the study of a membrane is to be made.
Probably, if a new cell had been used in the above
experiments, much better results would have been obtained
with the copper cobalticyanide membrane.   On account
of there being on hand at the time only a limited
number of available cells, and the desirability of
making the measurements of pressure recorded in the first
part of this paper, the author could not pursue the
study further.   While the experiments made with the
copper cobalticyanide membrane do not settle finally

the question of the possibility of using the membrane
for the measurement of osmotic pressure, the conclusion
seems warranted that this membrane is inferior to the
membrane of copper ferrocyanide.

The account above given of a few experiments
with the membrane is offered as a further contribution
to the knowledge of the subject, which it is hoped will
be of service when the study of the membrane of copper
cobalticyanide is continued.

BIOGRAPHICAL SKETCH.

Ernest Jenkins Hoffman was born at Jacksonport, Arkansas, April 4, 1879.

Since 1881, his home has been at Dallas, North Carolina, where he received his preparatory education, at Gaston College.   In the Fall of 1897, he entered Davidson College, North Carolina, from which he was graduated, in 1900, with the degree of Bachelor of Arts.

In October, 1901, he entered the Johns Hopkins University as a student in physics and mathematics. Since 1902, he has been a graduate student in chemistry, with physical chemistry and physics as his subordinate subjects.   Throughout his connection with the university he has held a North Carolina Hopkins Scholarship.